Mathematical Modelling of Carbonisation Process in Stamp Charged Coke Ovens

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Abstract

In this study, mathematical models of coal carbonisation in the coke oven have been developed. Models for thermo-physical properties(e.g. specific heat, density, and thermal conductivity) and heat of carbonisation reaction of coal during thermal decomposition to coke have been constructed in terms of the changes in the chemical composition and structure. To have sufficient generality for the applications to coke oven practices, the model describes the kinetics of release of main volatile matter constituents, thereby permitting the changes in the mass and composition of solid residue to be estimated by element balances. Correlations for the parameters of the models are derived so that prediction of volatile matter evolution can be made from coal ultimate analysis and heating profile. The computer based model predictions are in reasonable agreement with the experimental data generated by conducting pertinent experiments and literature information.

Key words: Coke oven, carbonization, mathematical model, volatile evolution, thermo-physical property, heat of reaction

Introduction

Commercial production of coke is a part of virtually every integrated steel making operation. The production of pig iron in the blast furnace utilises coke as both the fuel to generate the high temperatures required to produce separate liquid pig iron and slag phases and the carbon source for reducing the solid oxides. In view of the techno-economics of pig iron production, steel plants throughout the world have installed blast furnaces of large capacities. These furnaces have placed heavy demands on the quality of coke and in particular the Coke Strength after Reaction (CSR), Coke Reactivity Index (CRI) and Micum Indices in order to ensure low reactivity and high strength at elevated temperatures. Although, most of the coke ovens in the world follow the top charging route, some plants in India and abroad have adopted the stamp charging technology for production of coke for blast furnace operation. The compulsions of adopting the latter route arose from the lack of reserves of good quality coking coal in India, the coke produced, thus is detrimental to blast furnace operation and stability in view of it's poor CSR and Micum indices. The stamp charging method results in gainful utilisation of poor coking coals suitably blended with imported coals with better coking characteristics.

Coke oven carbonisation

The carbonisation process during coke-making has remained basically invariant for a long time. Coal, crushed so that about 80% of the particles are less than 3 mm in diameter, is either charged from the top or stamp charged using stamp-charging and pushing (SCP) machine into slot-type ovens. A battery can contain several ovens. The ovens are heated indirectly through the side walls which are usually made of silica refractory brick. Between the walls of adjacent ovens are flues through which the combustion products of the fuel gas pass, maintaining the oven wall at a temperature in the range 1100°C to 1300°C. Fig.1 & 2 show respectively the stamp-charged with SCP machine and top charged coke oven batteries in an integrated steel plant.

The charge temperature history is of significant importance, together with the stages of carbonisation. The coal near the oven walls is heated rapidly and heat is then gradually transmitted through the charge. When the charge attains 100°C, the moisture is considered to be converted to steam. As the temperature increases rapidly and the charge attains temperature between 350°C and 400°C, a good coking coal will soften and then begin to decompose. As heating continues, the particles coalesce to form a coherent porous structure. The duration of this plastic stage is comparatively short, generally lasting little more than 100°C, after which re-solidification takes place. The resulting semi-coke contracts, setting up differential strains and causing fissures to form perpendicular to the side walls. As the contraction occurs, volatile matter continues to be evolved and the semi-coke is gradually transferred into a brittle coke. When the charge centre temperature has

reached 900°C, a further period of up to three hours is allowed as a heat soak, the total carbonising time can vary between 18-24 hours.

Fig. 1: Stamp-charged coke ovens

Fig. 2: Top-charged coke ovens

Mathematical modelling framework
Volatile matter evolution

The kinetics of volatile matter release can be described by a system of parallel first-order reactions[1, 12, 13] for which the rate constant varies with the temperature according to Arrhenius relationship in a generalised framework.

$$\frac{d\delta}{dt} = [K \exp(-E/RT](1-\delta) \quad .....1$$

Where, δ is the fraction of the component of volatile matter released by time t, is the frequency factor, E is the activation energy, R is the gas constant and T, is the temperature in Kelvin(K). Each of the volatile matter species can be subdivided into components corresponding to different activation energies and the release of each of these components is assumed to be described by equation(1). The activation energies[1] for the volatile matter species, did not, in general, correspond closely to Gaussian distribution and a transformed Rossin-Rammler function has been used instead to describe the distribution[1]

$$F_j(E) = Exp\ \{-((E-E_0)/\alpha)^{\beta}\}; (j=1,N) \quad .....(2)$$

E_0 the 'starting activation energy', α and β vary both with species and coal rank. N is the number of species considered in the volatile matter. For the j_{th} volatile matter species, the cumulative amount m_j expressed as a fraction of dry ash free(*daf*) coal released at a time t is given by

$$m_j(t) = \overline{m_j} \int_0^1 \delta(t,E)\, dF_j(E)\, dE = \quad ....(3)$$

$$\overline{m_j} \int_{E_o}^{\infty} \delta(t,E) \frac{dF_j(E)}{dE} dE \ ;\ (j=1,2 \ldots N)$$

where, $\overline{m_j}$ are the final yields(as mass fraction of daf coal) of coke for the j number of species.

Therefore, the rate of release of species is given by,

$$\frac{dm_j}{dt} = \overline{m_j} \int_0^{\infty} \frac{\partial \delta}{\partial t} \frac{dF_j(E)}{dE} dE \ ;(j = 1,2 \ldots N) \quad ....(4)$$

Equations (3) and (4) can be solved by numerical method to predict the kinetics of release of the number of volatile matter species considered in the model.

The cumulative masses of the volatile matter species, $m_j(t)$, j=1, *N*, at time t calculated from equation(3) can be used to determine the mass of char remaining at time t, $m_o(t)$ by an overall mass balance

$$m_o(t) = 1 - \sum_{j=1}^{N} m_j(t) \quad ....(5)$$

The composition of the char residues at time t can be calculated by element balances and the details are available in the published literature[1]. In the present analysis, primary volatile matter is defined as Tar, CH_4, C_2H_6, H_2O, CO_2, NH_3 and H_2S). However, CH_4, C_2H_6 can be represented as C_mH_n, therefore, N has been taken as 6(N=6) as the number of species considered in all pertinent equations having the pecies index N. Previous experimental studies have[5,6] established that the evolution of the first five of these species occur below 550°C. Although investigations have shown that some hydrocarbons and CO_2 are still present above 600°C, the quantities are small and these species are not included as primary volatile matter. Because, the release of volatile matter occurs rapidly, changes in composition only have a transient effect on the prediction of semi-coke composition. It is, therefore, assumed in the model that the primary volatile matter can be treated as a mixture of constant composition, the release of which can be described by single reaction given above. As noted in previous studies1, that proportions of secondary volatile matter species produced above 600°C cannot be

assumed constant. Methane predominates at the lower temperature, where as hydrogen becomes important in the final stages of carbonisation.

Prediction of physical properties of the charge

The development of general mathematical models to describe changes of thermo-physical properties of coal during carbonisation has received little attention, in spite of the importance of these parameters in understanding and describing the thermal processes of coal during carbonisation. Any comprehensive heat transfer model of coke oven requires appropriate sub-models to evaluate thermo-physical properties of the charge, such as bulk density, specific heat, and thermal conductivity during carbonisation and heats of carbonisation towards the final stages of carbonisation cycle(beyond 700°C). In order to provide estimates for the wide range of conditions which can occur in coke oven charge, a series of mechanistic models based on published data have been developed.

Models for true density and porosity of the charge are also under development, because of the effect of these parameters on heat transfer by conduction and convection. The models of these properties are based on the yield and composition of the char residue and can, therefore be linked to the kinetic model of volatile matter evolution. In general, changes in the physical properties during carbonisation are thought to result from the chemical changes occurring, although in some cases (e.g. specific heat and thermal conductivity) temperature may also be an independent variable. The models for thermo-physical properties are based on changes in chemical composition predicted by the kinetic model of volatile matter evolution. This enables the thermo-physical properties during carbonisation to be related to the composition of the initial coal and heating condition. Here, a brief description of the formalism is presented.

Bulk Density

The loss of volatile matter results in a reduction in the average bulk density of the charge, although some shrinkage also occurs during carbonisation. The bulk density, q, of an element of charge is given by

$$\rho = \rho_0 Y/(1+\varepsilon V) \quad ....(6)$$

Where, ρ_0 is the initial (wet) bulk density of the charge. Y is the yield of the coke (per mass of initial charge) and εV is the fractional volume changes of the charge ($\varepsilon V \therefore 0$ implies shrinkage). The details of formulations and methodology of evaluation of the bulk density is reported elsewhere [8,9] which need not be repeated.

Heats of Reaction

The heats of exothermic reactions during carbonisation[7] can be given by the following equation for the rate of release of heat(dq/dt) under isothermal conditions at temperature T°C.

$$\frac{dq}{dt} + \sum_{j=0}^{N} \frac{d}{dt}(u_j m_j) = 0 \quad ...(7)$$

Where, q is the heat release, daf coal basis, u_j,(j=0, 1, 2, 3, 4, 5, …N), are heats of formation at temperature T and m_j,(J= 0, 1,2…..N), are the mass fractions of carbonisation products daf coal basis. The index, j=0, 1…..N+1 refers to char and the volatile matter species considered in the model of volatile matter evolution. The heats of formation at temperature T°C for the volatile matter species can be approximated as a quadratic function of temperature [7, 8, 13, 14]:

$$u_j = \sum_{k=0}^{2} P_{jk} T^K \quad ....(8)$$

The coefficients of P_{jk} were derived from standard tables of physical and chemical properties. For the char the heat of formation can be calculated from the standard heat of combustion using Hess's and Kirchoff's law [7, 11, 13, 14]:

$$u_o = H - \sum_{c=1}^{5} \phi_i y_i + \Delta h \quad ....(9)$$

Where, H= Heat of combustion at 25°C, ϕ_i (i=1,…5) are constants representing the heats of combustion of above elements C, H, O, N and S respectively(at 25°C) and Δh is the change in enthalpy from 25 to T°C. The values of the coefficients ϕ_i are available in the standard tables. The correlation of Mott and Spooner [7, 8] has been used to evaluate heats of combustion of coal and coke in terms of their ultimate analysis.

$$H = \sum_{c=1}^{5} \lambda_i y_i \quad ...(10)$$

Where y_i are the mass fractions of carbon, hydrogen, oxygen, nitrogen and sulphur on daf basis, and λ_i are known constants.[7,11] The enthalpy changes from 25 to T°C for the coal, char or coke can be given as:

$$\Delta h = \sum_{c=1}^{5} \left(y_i / \mu_i\right) f(\bar{T}) \quad ....(11)$$

And 7, 8, 9 μ_i are the respective atomic weight of the elements C, H, O, N and S (12, 1, 16, 14 and 32).

$$f(\bar{T}) = R\left(380\ g_o\left(380/T\right) + 3600 g_o\left(1800/T\right) - 156\right) \quad ....(12)$$

After substituting in the above equations in the rate equation for heat release, and with simplification:

$$\frac{dq}{dt} + \sum_{i=1}^{5} (\lambda_i - \phi_i + f(\overline{T})/\mu_i) \frac{d}{dt}(m_o y_i) + \quad .....(13)$$

$$\sum_{j=1}^{N} (\sum_{k=0}^{2} P_{jk} T_k) \frac{dm_j}{dt} = 0$$

The heat release can be expressed in terms of release rate can also be expressed as:

$$\frac{dq}{dt} = \sum_{j=1}^{N} \frac{\partial q}{\partial m_j} \frac{dm_j}{dt} \quad ....(14)$$

where,

$$\frac{dq}{dt} = \sum_{i=1}^{5} A_{ij} (\lambda_i - \phi_i + f(\overline{T})/\mu) - \sum_{K=0}^{2} P_{jK} T^K \quad .....(15)$$

Specific Heat

The approach adopted to model the specific heat of coal and coke is to apply Einstein form of quantum theory specific heat description for solids[7,10] it was not until the development of quantum theory that a satisfactory explanation for the temperature dependence of specific heat was found. The Einstein model of specific heat assumes that the atoms oscillate independently in three dimensions with a common characteristic frequency. The theory leads to the following expressions for the specific heat.

$$C=3R(E(T_K/ \text{ᔓ}E) \quad .....(16)$$

Where, ᔓE is the characteristic Einstein temperature of the solid (K). TK is the temperature (K) and the function E(y) is the Einstein function for specific heat, defined as:

$$E(y) = e^{1/y}/(y(e^{1/y}1)^2 \quad .....(17)$$

Although a more accurate specific heat model was subsequently developed by Debye, this has not been used in the present study because small improvements in accuracy for the temperatures of interest are not considered to justify the extra computational complexity.

Effective Thermal Conductivity

It is assumed that that the main mechanism responsible for heat transfer in a coke oven charge can be described by an effective(overall) thermal conductivity comprising,

(a) Conduction through gas phase
(b) Conduction through the solid phase
(c) Radiation across interstices and pores
(d) Radiation across the cracks and fissures

The heat transfer coefficients for natural convection are usually small. This mechanism has therefore been excluded from the present study. In the early stages of carbonisation, a coke oven charge consists of coal particles surrounded by air or by the steam produced as the charge dries. The thermal conductivity is low as heat transfer between particles relies largely on conduction across the gas film. The formation, during plastic stage, of a continuous solid phase would therefore be expected to increase the thermal conductivity. Without elaborating the intermediate mathematical steps, the final expression for effective thermal conductivity [9,11,12,15] of the particulate charge may be summarised by the following equation:

$$K_{part} = w_2 k_3 + (1-w_2)/(\text{ᔓ}'/(k_1+k_2)+(1-\text{ᔓ}')/k_0) \quad .....(18)$$

Where, K_{part} = Overall effective thermal conductivity of the particulate charge

k_0, k_1, k_2 and k_3 are respectively contributions from solid conduction, gas conduction, radiation across the interstices and conduction through moisture and,

$$\text{ᔓ}' = 1-(1-e)\,0.5 \quad .....(19)$$

Where, ᔓ is the total charge porosity. Without elaborating the detailed mathematical steps,[9,11,12,15] the final expression for the effective thermal conductivity of the coke charge may be summarised by the following equation :

$$K_{coke} = (1-\text{ᔓ})k_0 + \text{ᔓ}k_1 + \text{ᔓ}_{int}k_{2a} + \text{ᔓ}_{ex}tk_{2b} \quad ....(20)$$

Where, ᔓ is the total charge porosity; eint the fraction of the charge volume occupied by internal pores; and eext = the fraction of the charge volume occupied by the fissures and cracks.

For simplicity, the changeover from the particulate charge model to coke charge is assumed to occur at the re-solidification temperature. Since the density and porosity calculations are based on the models for volatile matter evolution, the charge thermal conductivity may be estimated from the proximate and ultimate analysis of coal, the initial bulk density and heating profile.

Model Implementation

For the implementation of the mathematical models, an in-house interactive FORTRAN code named *COKESIM-1* developed to solve the equations of the model numerically for constant heating rate conditions. After acquisition and preliminary processing of the input data for typical Indian coal used in steel works, the code calculates the final yields of primary volatile matter and secondary volatile matter on dry ash free basis. The code then enters an iterative loop in which the temperature is increased from 3500C in the steps as desired by the user. At each stage of the iteration, the masses in primary volatile matter and the cumulative yields of the three secondary volatile matter species are revised. The semi-

coke yield and composition are calculated by mass balance on the five elements present and used to predict the mean relative atomic mass of the semi coke.

The *COKESIM-1* code, which calculates the yields and composition of the volatile matter and semi-coke composition, has been extended, using the models of physical properties to calculate the physical properties of the charge during coke oven carbonisation. This extended in-house interactive FORTRAN code has been named as *COKESIM-2.* The code requires as input, the ultimate analysis of the coal, the conditions of the coal as charged (i.e. moisture, ash, bulk density, temperature etc.) and the heating rate (assumed constant). The code calculates all the required physical properties of the charge during carbonisation. The calculations are carried out in an iterative loop in which the temperature is increased at a constant rate. The calculation for each of the physical properties' models is based on the predictions of volatile matter evolution and temperature alone. The results can be printed at the end of each iteration. Execution of the program terminates when the temperature reaches the specified final value.

Results and Discussion

The predicted primary and secondary volatile matter yield (daf initial coal basis) are shown in Figs. 3 & 4 respectively. The predicted total yield of volatile matter (at 3°C/min) is shown in Fig. 5. The evolution of primary volatile matter appears to be complete by 600°C, although the secondary volatile matter species continue to be released at 1000°C. The cumulative matter yield is validated with the Thermo-Gravimetric Analysis (TGA) experiment conducted by the investigators with the identical Indian coal sample and also with the experimental investigations published and widely referred literature[1,7,8,9] for top charged coke oven carbonisation. Literature for stamp charged coke ovens are extremely scanty. In principle, the basic process phenomenology for both stamp charged and top charged batteries are intrinsically similar except the charge density and moisture content of the charge. These literature references have been cited in all subsequent results and graphs for comparison, wherever applicable. Fig.6 shows the variation of carbon and hydrogen content of the charge as carbonisation process progresses. The predicted pattern of the total volatile matter release is in reasonable general agreement with that observed experimentally. In particular, the model reproduces the rapid evolution of primary volatile matter between 400°C and 500°C.

The predicted variation of the final yields of the main hydrogen containing species with coal type is consistent with the preferential loss during coalification of those species having the lowest activation energy. As the hydrogen content of the coal is reduced during coalification, it is the yield of the tar which falls, rather than the yields of CH_4 or H_2. The model takes into account the kinetics of primary volatile matter release. Because of the wide range of temperatures over which secondary volatile matter release occurs, the evolution of these species is not described kinetically in the present model. The evolution of three secondary volatile a matter species (CH_4, H_2, CO) occurs simultaneously. In the fig.4, the markers indicate the yield of different volatile species as predicted by the mathematical model. Although each may be the final product of a complex sequence of reactions, it is assumed in the model that their evolution can be considered independently.

Fig. 7 shows that most of the exothermic heat release during carbonisation is predicted as occurring above 800°C which is in agreement with the experimental observations in the earlier cited published literature. The reactions responsible for the centre of a coke oven charge becoming hotter than the walls towards the end of carbonisation do occur at high temperature which is consistent with the model predictions. The heat release does not occur, however, until the reactive intermediate semi-coke produced by the release of secondary volatile matter is converted into mature coke. Fig. 8 shows the variation of effective (overall) thermal conductivity of the coke oven charge as a function of temperature. The thermal conductivity increases slowly up to 400°C then accelerates rapidly as shown in Fig. 8. The solid thermal conductivity increases slowly until decomposition begins, after which a rapid increase occurs until the thermal conductivity of mature coke is approached. The gas thermal conductivity also increases after the onset of volatile matter evolution because the thermal conductivity of hydrogen is considerably greater than that of the air or steam initially present. The effective thermal conductivity due to radiation increases as a cube of the absolute temperature, while the heat flux increases as fourth power of absolute temperature. Solid conduction, gas conduction and radiation all contribute to the effective thermal conductivity of a coke oven charge. Gas conduction limits the rate of heat transfer during the particulate charge, whereas radiation along the fissures becomes the major mechanism in the final stages of carbonisation.

As shown in Fig. 9, the present model predicts a relatively rapid increase in specific heat between ambient temperature and 400°C followed by a decrease between 500°C and 1000°C. The existence of a maximum specific heat at 400°C to 500°C is thought to be responsible for the apparent endothermic reactions occurring in this temperature range. In the case of 25-30%, volatile matter coal, the decrease in the specific heat value from the maximum value to that at 1000°C is 13%. The initial increase in the specific heat is attributable to the effect of temperature alone. Until decomposition begins, the

specific heat increases asymptotically to the maximum value. The variation of specific heat with temperature has been described by Einstein's model and with composition by assuming that the vibrational energy at any temperature is the same for each atom. When used with the model of volatile matter evolution to predict the specific heat of the coal during carbonisation, it was found that the specific heat rises rapidly to a maximum value at 400°C to 500°C, subsequently to the Dulong & Petit limiting value for carbon at high temperature. The predicted decrease in the bulk density during carbonisation occurs because of the mass loss resulting from volatile matter and the removal of moisture. The major change in bulk density therefore occurs at 100°C and during the primary volatile matter evolution stage. The shrinkage of the coke formed near the oven wall is likely to reduce the bulk density of the coke formed at the oven centre. This effect is not taken into account in the present model, which calculates average bulk density of the oven charge. The broad trend of bulk density variation as a function of charge temperature predicted by the present model (stamp charged oven) and the literature reference (top charged oven) are quite consistent.

Conclusion

A model of volatile matter evolution in which the yield and composition of the volatile matter was predicted as a function of temperature from the ultimate analysis of the coal and the heating rate for stamp-charged coke ovens. The model considers the evolution of the following species, primary volatile matter, methane, carbon monoxide and hydrogen. The evolution of these species is governed by parallel first order decomposition reaction, the rate constant for which depend on a distribution of activation energies. The final yields of the species and composition of the primary volatile matter are estimated from the ultimate analysis of the coal by appropriate correlations. The predictions of the model and their broad trends are in good agreement with the published literature information and experimental data. A heat balance model relating the heat release at any stage of carbonisation to the cumulative yield of volatile matter species has been developed. The actual heat release occurs as the semi-coke matures. The carbonisation heat release does not occur, until the semi-coke is converted to coke with the release of the volatile matter. A series of models relating the thermo-physical properties of the oven charge in conjunction with the change in chemical composition and structural characteristics has been developed. The models are based on fundamental principles and published correlation and, are constructed for use in conjunction with the volatile matter evolution model. These models provide mechanistic interpretation of the fundamental processes and published theoretical and experimental investigations. The main source of uncertainty in some of the predictions is attributed to lack of availability of comprehensive data base for Indian coals.

Reference

1. Merrick D, Fuel 1983, 62, p534
2. Osinski E. J., Barr P.V. and Brimacombe J.K., Ironmaking and Steelmaking 1993, 20(5), p350
3. Osinski E. J., Barr P.V. and Brimacombe J.K., Ironmaking and Steelmaking 1993, 20(6), p453
4. Barr P.V., Osinski E. J.,Brimacombe J.K.,Khan M.A. and Readthough P.J., Ironmaking and Steelmaking 1993, 21(1), p44
5. Millard D.J., J. Inst. Fuel, 1955, 28, p345
6. Merrick D, ISS Ironmaking Proc.,1982, 41, p289
7. Merrick D, Fuel, 1983, 62, p540
8. Merrick D, Fuel, 1983, 62, p547
9. Merrick D, Fuel, 1983, 62, p553
10. Voller V.R.,Cross M., and Merrick D., Fuel, 1983, 62, p562
11. Osinski E. J.,Brimacombe J..K., Barr P.V. and Khan M.A., Proc.2nd Int. "Cokemaking" Cong., 1992, 2, p374
12. Osinski E. J.,Brimacombe J.K., Barr P.V., Grandsen J.E. and Khan M.A., ISS Ironmaking Proc., 1992,51, p421
13. Chen K.L. and Chin M.Q., ISS Ironmaking Proc., 1986, 45, p279
14. Laurier G.C.,Readyhough P.J. and Sulivan G.R., Fuel, 1986, 65, p1190
15. Reilly A.M.,Readyhough P.J. and Sulivan G.R., Fuel, 1988, 67, p997

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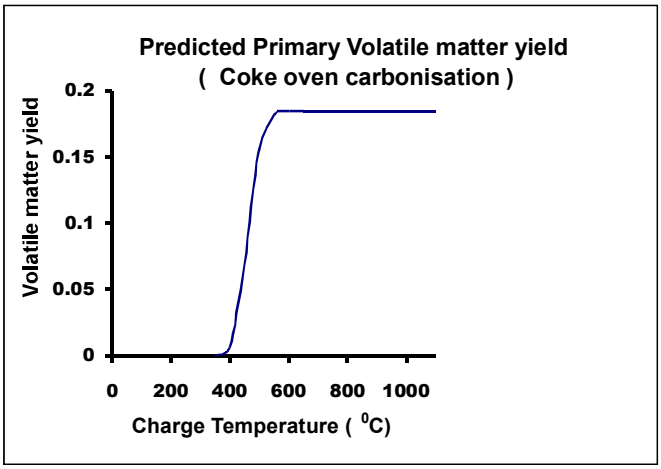

Fig. 3: Kinetic model prediction for primary volatile matter yield

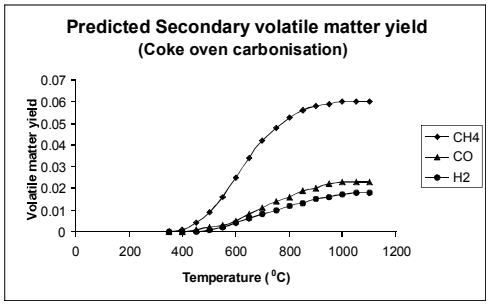

Fig. 4: Kinetic model predictions for secondary volatile matter yield

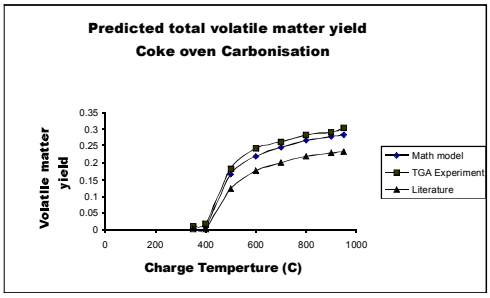

Fig. 5: Kinetic model predictions for total volatile Matter yield

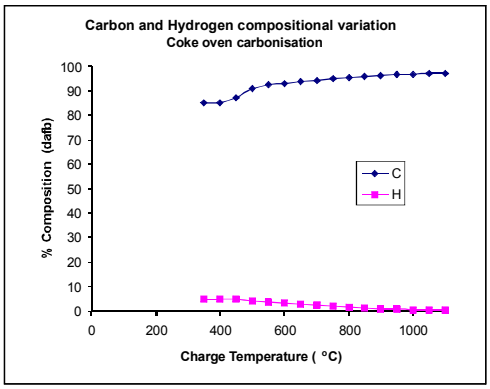

Fig. 6: Kinetic model predictions for variation of composition

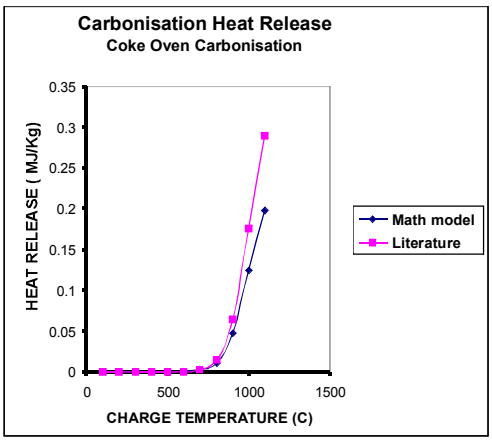

Fig. 7: Release of carbonisation Heat of reaction

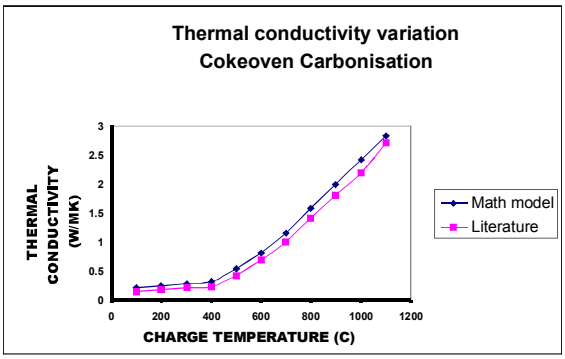

Fig. 8: Variation of effective(overall) thermal conductivity

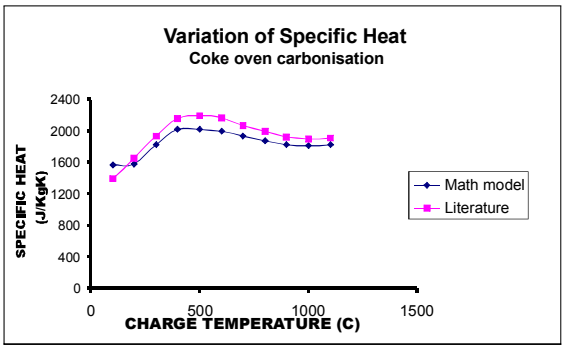

Fig. 9: Variation of specific heat with charge temperature Fig.10. Variation of bulk density with charge temperature

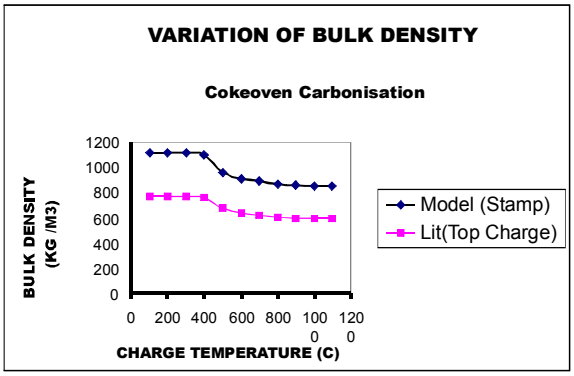

Fig.10: Variation of bulk density with charge temperature